

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁶ : C07F 7/08, 7/28, 7/00, 9/00, C08F 4/44, 4/642	A1	(11) International Publication Number: WO 99/14219 (43) International Publication Date: 25 March 1999 (25.03.99)
(21) International Application Number: PCT/US98/13095 (22) International Filing Date: 24 June 1998 (24.06.98) (30) Priority Data: 08/928,820 12 September 1997 (12.09.97) US (71) Applicant: PHILLIPS PETROLEUM COMPANY [US/US]; 4th and Keeler, Bartlesville, OK 74004 (US). (72) Inventors: JUNG, Michael; Postfach 101251, D-95440 Bayreuth (DE). ALT, Helmut, G.; Wacholderweg 27, D-95445 Bayreuth (DE). WELCH, Melvin, Bruce; 4750 Lewis Drive, Bartlesville, OK 74006 (US). (74) Agents: WEST, Paul, B.; Ladas & Parry, 26 West 61st Street, New York, NY 10023 (US) et al.		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: BRIDGE FLUORENYL/INDENYL METALLOCENES AND THE USE THEREOF		
(57) Abstract Bridged fluorenyl/indenyl metallocenes having substituents at the 3 position of the indenyl and the use thereof in the polymerization of olefins are disclosed. Also a new method for preparing bridged fluorenyl/indenyl ligands wherein the indenyl has a substituent in the 3 position and the preparation of metallocenes with such ligands.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

BRIDGE FLUORENYL/INDENYL METALLOCENES AND THE USE THEREOFField of the Invention

The present invention relates to metallocenes. In a more specific aspect the invention relates to particular types of bridged fluorenyl/indenyl metallocenes
 5 having unusual effectiveness as catalysts for the polymerization of olefins. In another aspect the invention relates to the use of such metallocenes in the polymerization of olefins. Still another aspect of the invention relates to a method for preparing bridged fluorenyl/indenyl ligands having certain substituents at the 3 position of the indenyl, which ligands can be used to prepare the metallocenes of the present invention.

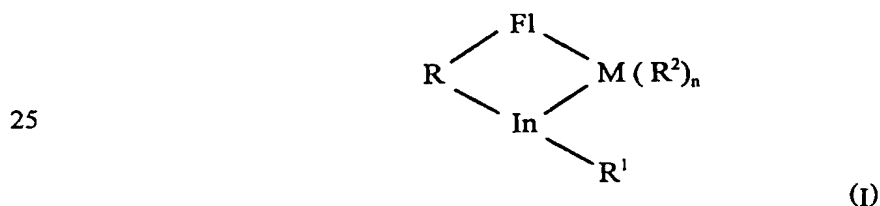
10 Background of the Invention

Metallocenes are unique in the field of olefin polymerization in that it has been discovered that by changing the substituents on the organic ligands of the metallocene it is often possible to change certain effects that the metallocenes have on the polymerization process. Examples of changes observed following some changes of
 15 substituents include polymerization activity, polymer molecular weight, and comonomer selectivity. The process of determining what effect changes in substituents will have is, however, still largely empirical.

The present invention provides certain bridged fluorenyl indenyl metallocenes that have improved properties as olefin polymerization catalysts.

20 Summary of the Invention

The present invention is concerned with bridged fluorenyl/indenyl metallocenes of the formula (I)



wherein R is a divalent organo radical connecting Fl and In, Fl is a 9-fluorenyl radical, In is an indenyl radical connected to R at the 1 position and to R¹ at the 3 position,
 30 wherein R and R¹ are the only substituents on In, wherein R¹ is selected from the group consisting of alkyl, aralkyl, alkenyl, alkylsilyl, alkenylsilyl, and alkoxyalkyl radicals having 1 to 20 carbon atoms, M is a metal selected from the group consisting

- 2 -

of titanium, zirconium, hafnium, niobium, and tantalum, and each R^2 can be the same or different and is selected from hydrogen, halides, alkyl radicals containing 1 to 10 carbon atoms, aryl radicals having 6 to 12 carbon atoms, alkenyl radicals having 2 to 10 carbon atoms, arylalkyl radicals having 7 to 40 carbon atoms, arylalkenyl radicals
5 having 8 to 40 carbon atoms, and alkylaryl radicals having 7 to 40 carbon atoms, n is a number to fill the remaining valences of M, further characterized by the fact that R^1 is not allyl or propenyl if R is dimethylsilyl.

Another aspect of the invention relates to a method for preparing bridged fluorenyl/indenyl ligands having certain substituents at the 3 position of the
10 indenyl, which ligands can be used to prepare the metallocenes of the present invention. Also in accordance with the present invention there is provided the process of using such metallocenes in the polymerization of olefins.

Detailed Description of the Invention

The bridge R of the metallocenes of the present invention can be
15 selected from any suitable divalent organo radicals, preferably those containing 1 to 20 carbon atoms. Some typical examples include dimethyl silyl, diphenyl silyl, phenyl methyl silyl, dimethyl methylene, 1-methyl-1-phenyl methylene, diphenylmethylene, alkenyl substituted ethylenes having 4 to 12 carbon atoms, alkyl substituted ethylenes having 4 to 12 carbon atoms, and unsubstituted ethylene, i.e. 1,2-ethylene. It is
20 currently preferred that the fluorenyl radical be unsubstituted. The term methylene and ethylene as used herein are also sometimes referred to as methylidene and ethylidene, respectively.

Most of the metallocenes of the present invention can be produced by preparing the necessary organic ligand and then reacting the dilithium salt of the ligand
25 with a suitable metal compound using techniques known in the art. Various techniques can be used to prepare the necessary organic ligand. One inventive technique involves reacting lithium fluorenyl with a benzofulvene in diethylether to produce a bridged fluorenyl/indenyl ligand lithium salt which is then reacted with an alkyl, alkenyl, or organosilyl halide to result in a bridged fluorenyl/indenyl ligand having the
30 corresponding alkyl, alkenyl, or organosilyl halide in the 3 position on the indenyl.

After the reaction of the ligand salt with the metal compound the metallocene can be recovered and purified using conventional techniques known in the

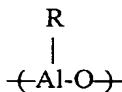
- 3 -

art such as filtration, extraction, crystallization, and recrystallization. It is generally desirable to recover the metallocene in a form that is free of any substantial amount of by-product impurities. Accordingly, recrystallization and fractional crystallization to obtain relatively pure metallocenes is desirable. Dichloromethane has been found to be particularly useful for such recrystallizations. Since the stability of the various metallocenes varies, it is generally desirable to use the metallocenes soon after their preparation or at least to store the metallocene under conditions favoring their stability. For example the metallocenes can generally be stored in the dark at low temperature, i.e. below 0°C, in the absence of oxygen and water.

The resulting inventive indenyl-containing metallocenes can be used in combination with a suitable cocatalyst for the polymerization of olefinic monomers. In such processes the metallocene or the cocatalyst can be employed on a solid insoluble particulate support. In a preferred process when the metallocene has a polymerizable group the metallocene is prepolymerized in the presence of the cocatalyst using the technique taught in U.S. Patent 5,498,581. Preferably the prepolymerization is conducted in the presence of a particulate diluent such as silica or polyethylene.

Examples of suitable cocatalysts include generally any of those cocatalysts which have in the past been employed in conjunction with transition metal containing metallocene olefin polymerization catalysts. Some typical examples include organometallic compounds of metals of Groups IA, IIA, and IIIB of the Periodic Table. Examples of such compounds have included organometallic halide compounds, organometallic hydrides and even metal hydrides. Some specific examples include triethyl aluminum, triisobutyl aluminum, diethyl aluminum chloride, diethyl aluminum hydride, and the like.

The currently most preferred cocatalyst is an aluminoxane. Such compounds include those compounds having repeating units of the formula



where R is an alkyl group generally having 1 to 5 carbon atoms.

Aluminoxanes, also sometimes referred to as poly(hydrocarbyl aluminum oxides) are well known in the art and are generally prepared by reacting an organo

- 4 -

hydrocarbylaluminum compound with water. The currently preferred cocatalysts are prepared either from trimethylaluminum or triethylaluminum, sometimes referred to as poly(methyl aluminum oxide) and poly(ethyl aluminum oxide), respectively. It is also within the scope of the invention to use an aluminoxane in combination with a
5 trialkylaluminum, such as disclosed in U.S. Patent No. 4,794,096.

The indenyl-containing metallocenes in combination with the aluminoxane cocatalyst can be used to polymerize olefins, especially alpha olefins having 2 to 12 carbon atoms. Often such polymerizations would be carried out in a homogeneous system in which the catalyst and cocatalyst were soluble; however, it is
10 within the scope of the present invention to carry out the polymerizations in the presence of supported or insoluble particulate forms of the catalyst and/or cocatalyst. The catalyst is thus considered suitable for solution, slurry, or gas phase polymerization. It is within the scope of the invention to use a mixture of two or more of the inventive indenyl-containing metallocenes or a mixture of an inventive indenyl-
15 containing metallocene with one or more other cyclopentadienyl-type metallocenes.

The indenyl-containing metallocenes when used with aluminoxane are particularly useful for the polymerization of ethylene in the presence or absence of other olefins. Examples of other olefins that might be present include mono-unsaturated aliphatic alpha-olefins having 3 to 10 carbon atoms. Examples of such
20 olefins include propylene, butene-1, pentene-1, 3-methylbutene-1, hexene-1, 4-methylpentene-1, 3-methylpentene-1, heptene-1, octene-1, decene-1, 4,4-dimethyl-1-pentene, 4,4-diethyl-1-hexene, 3-4-dimethyl-1-hexene, and the like and mixtures thereof.

The polymerizations can be carried out under a wide range of conditions
25 depending upon the particular metallocene employed, and the results desired. Examples of typical conditions under which the metallocenes can be used in the polymerization of olefins include conditions such as disclosed in U.S. Patents 3,242,099; 4,892,851; and 4,530,914. It is considered that generally any of the polymerization procedures used in the prior art with any transition metal based catalyst
30 systems can be employed with the present inventive indenyl-containing metallocenes.

The amount of cocatalyst can vary over a wide range. It is currently preferred for the molar ratio of the aluminum in the aluminoxane to the transition

- 5 -

metal in the metallocene to be in the range of about 0.1:1 to about 100,000:1 and more preferably about 5:1 to about 15,000:1. In many cases, the polymerizations would be carried out in the presence of liquid diluents which do not have an adverse affect upon the catalyst system. Examples of such liquid diluents include propane, butane, isobutane, pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane, toluene, xylene, and the like. The polymerization temperature can vary over a wide range, temperatures typically would be in the range of about -60°C to about 300°C, more preferably in the range of about 20°C to about 160°C. Typically the pressure would be in the range of from about 1 to about 500 atmospheres or greater.

The polymers produced with this invention have a wide range of uses that will be apparent to those skilled in the art from the physical properties of the respective polymer.

A further understanding of the present invention and its objects and advantages will follow from the following examples.

Example 1

Synthesis of Omega Alkenyl Silyl Indene and other Indenes

Dimethyl chlorosilane was reacted with an excess 1,5-hexadiene in the presence of a platinum catalyst to form dimethyl-5-hexenylchloro silane. Then indene was reacted with butyl lithium in a mixture of diethyl ether and tetrahydrofuran to produce the indenyl lithium salt which was then reacted with the dimethyl-5-hexenylchlorosilane to yield the omega alkenyl dimethyl indene which can be called 5-hexenyl-dimethyl-silyl-1-indene.

Other substituted indenenes were prepared by substituting other organohalides for the above dimethylindenyl-5-hexenylchloro silane. The substituted indenenes prepared included allyl-1-indene, 3-butenyl-1-indene, 4-pentenyl-1-indene, 5-hexenyl-1-indene, butyl-1-indene, hexyl-1-indene, and benzyl-1-indene.

Example 2

Synthesis of Dihydrocarbyl Silyl Bridged Fluorenyl Indenyl Ligands

An unsubstituted indenyl or one of the 1-substituted indene compounds prepared in Example 1 were employed to produce silyl bridged ligands having fluorenyl and indenyl groups. This was done by reacting the respective indenyl with butyl lithium in diethyl ether to form the corresponding indenyl lithium compound. A

- 6 -

dihydrocarbyl dichlorosilane was reacted with fluorenyl lithium in pentane to produce the corresponding 9-fluorenyl dihydrocarbyl chlorosilane. Then the 9-fluorenyl dihydrocarbyl chlorosilane was combined with the indenyl lithium compound and stirred overnight. The mixture was hydrolyzed and dried over sodium sulfate and the organic phase dried using a vacuum. For purification the organic product was dissolved in pentane and filtered over silica gel. This general process produced the following ligands:

- 9-fluorenyl-1-indenyl dimethyl silane
- #9-fluorenyl-1-(3-allyl)indenyl dimethylsilane
- 10 9-fluorenyl-1-(3-but-3-enyl)indenyl dimethylsilane
- 9-fluorenyl-1-(3-pent-4-enyl)indenyl dimethylsilane
- 9-fluorenyl-1-(3-hex-5-enyl)indenyl dimethylsilane
- 9-fluorenyl-1-(3-hex-5-enyl-dimethyl-silyl)indenyl dimethylsilane
- 9-fluorenyl-1-(3-benzyl)indenyl dimethylsilane
- 15 9-fluorenyl-1-(3-butyl)indenyl dimethylsilane
- 9-fluorenyl-1-(3-hexyl)indenyl dimethylsilane

Example 3

Preparation of Substituted Benzofulvenes

6,6-dimethyl benzofulvene was prepared by dissolving 0.14 mmol of indene with 0.17 mmol of dimethylketone in 60 ml of methanol and 0.17 mmol of pyrrolidine. The reaction mixture was stirred over night and then reacted with 11.5 ml (0.2 mol) glacial acetic acid and extracted by shaking with water and pentane. The organic phase was dried under a vacuum and distilled under high vacuum to yield 6,6-dimethyl-benzofulvene. A similar technique was used to prepare 6-methyl-6(3-butenyl)-benzofulvene using the methyl-(3-butenyl) ketone.

In another process 0.14 mol of sodium dust was added to 60 ml of ethanol. Then 0.14 mol of methyl phenyl ketone was added. Then 0.28 mol of indene was added dropwise and the mixture stirred for 15 hours under reflux. The resulting product was then diluted with water and extracted with pentane, the organic phase evaporated, the excess indene removed using HV distillation and the residue dissolved in pentane and filtered over silica gel to produce 6-methyl-6-phenyl-benzofulvene. A similar process was used to produce 6,6-diphenylbenzofulvene.

- 7 -

Example 4Preparation of C₁ Bridged Ligands

First 36 mmol of fluorene was dissolved in 100 ml of diethylether and slowly mixed with 36 mmol of n-butyl lithium provided via a 1.6M hexane solution at room temperature. The reaction mixture was stirred for several hours. Then an equimolar amount of a substituted benzofulvene was added and the mixture stirred overnight. Then the mixture was hydrolyzed with 50 ml of water, the organic phase dried over sodium sulfate and the solvent evaporated under vacuum. The residue was dissolved in pentane, the solution filtered over silica gel and crystallized at -18°C.

This process produced the following ligands:

- 2-(9-fluorenyl)-2-(1-indenyl)propane
- 1-(9-fluorenyl)-1-(1-indenyl)-1-phenylethane
- 5-(9-fluorenyl)-5-(1-indenyl)-1-hexene

In another process 36 mmol of fluorene was dissolved in 100 ml of diethylether and mixed with 36 mmol n-butyl lithium provided via a 1.6M hexane solution and then stirred for several hours. An equimolar amount of a benzofulvene is added and the mixture stirred over night. Then the mixture was cooled down to -78°C and 36 mmol of a hydrocarbyl halide such as an alkyl, alkenyl, or organo silyl halide was added and the mixture stirred for 15 hours at room temperature. The reaction mixture was then hydrolyzed with 50 ml of water and the organic phase dried over sodium sulfate and the solvent evaporated under vacuum. For purification the residue was dissolved in pentane, the solution filtered over silica gel and crystallized at 18°C. This technique was used to prepare the following ligands:

- 2-(9-Fluorenyl)-2-[1-(3-allyl)-indenyl]propane
- 2-(9-Fluorenyl)-2-{1-[3-(3-butenyl)]-indenyl}propane
- 2-(9-Fluorenyl)-2-{1-[3-(4-pentenyl)]-indenyl}propane
- 2-(9-Fluorenyl)-2-{1-[3-(5-hexenyl)]-indenyl}propane
- 2-(9-Fluorenyl)-2-[1-(3-trimethylsilyl)-indenyl]propane
- 2-(9-Fluorenyl)-2-[1-(3-allyldimethylsilyl)-indenyl]propane
- 2-(9-Fluorenyl)-2-{1-[3-(5-hexenyldimethylsilyl)]-indenyl}propane
- 2-(9-Fluorenyl)-2-[10(3-butyl)-indenyl]propane
- 2-(9-Fluorenyl)-2-[1-(3-hexyl)-indenyl]propane

- 8 -

- 2-(9-Fluorenyl)-2-{1-[3-(2-methoxyethyl)]-indenyl}propane
 2-(9-Fluorenyl)-2-[1-(3-methyldiphenylsilyl)-indenyl]propane
 2-(9-Fluorenyl)-2-[1-(3-benzyl)-indenyl]propane
 2-(9-Fluorenyl)-2-{1-[3-(2-phenyl-ethyl)]-indenyl}propane
 5 1-(9-Fluorenyl)-1-[1-(3-allyl)-indenyl]-1-phenylethane
 1-(9-Fluorenyl)-1-{1-[3-(3-butenyl)]-indenyl}-1-phenylethane
 1-(9-Fluorenyl)-1-{1-[3-(4-pentenyl)]-indenyl}-1-phenylethane and isomer
 1-(9-Fluorenyl)-1-{1-[3-(5-hexenyl)]-indenyl}-1-phenylethane and isomer
 1-(9-Fluorenyl)-1-[1-(3-butyl-indenyl)]-1-phenylethane and isomer
 10 1-(9-Fluorenyl)-1-[1-(3-hexyl)-indenyl]-1-phenylethane and isomer
 1-(9-Fluorenyl)-1-[1-(3-benzyl)-indenyl]-1-phenylethane and isomer
 1-(9-Fluorenyl)-1-{1-[3-(2-phenyl-ethyl)]-indenyl}-1-phenylethane and isomer
 1-(9-Fluorenyl)-1-[1-(3-trimethylsilyl)-indenyl]-1-phenylethane and isomer
 1-(9-Fluorenyl)-1-[1-(3-allyldimethylsilyl)-indenyl]-1-phenylethane and isomer
 15 1-(9-Fluorenyl)-1-{1-[3-(2-methoxyethyl)]-indenyl}-1-phenylethane and isomer
 5-(9-Fluorenyl)-5-[1-(3-trimethylsilyl)-indenyl]-1-hexene and isomer
 5-(9-Fluorenyl)-5-{1-[3-(3-butenyl)]-indenyl}-1-hexene and isomer

Example 5

Preparation of Ethylidene Bridged Ligands

- 20 A series of ethylene bridged indenyl/fluorenyl ligands having omega
 alkene branches off the ethylene bridge were prepared by reacting various
 1,2-epoxyalkenes with fluorenyl lithium to obtain the corresponding 1-fluorenyl-
 omega-alkenyl-2-ol. Then mesyl chloride, i.e., methane sulfonyl chloride, was added
 to that compound in the presence of trimethylamine and methylene chloride to produce
 25 the corresponding 1-fluorenyl-omega-alkenyl-2-mesylate. The mesylate was then
 reacted with indenyl lithium in diethyl ether and then hydrolyzed with water to
 produce the ligand. This process was used to produce the following ligands:
 6-(9-fluorenyl)-5-(1-indenyl)-1-hexene
 8-(9-fluorenyl)-7-(1-indenyl)-1-octene
 30 10-(9-fluorenyl)-9-(1-indenyl)-1-decene

Inventive fluorenyl/indenyl ethylene bridged ligands with substituents on
 the 3 position of the indenyl were prepared by reacting the substituted indenyl lithium

- 9 -

compound with 1-bromo-2-(9-fluorenyl) ethane, hydrolyzing, and recovering and purifying. This process was used to produce the following ligands:

- 1-(9-fluorenyl)-2-(1-(3-allyl)indenyl)ethane
- 1-(9-fluorenyl)-2-(1-(3-but-3-enyl)indenyl)ethane
- 5 1-(9-fluorenyl)-2-(1-(3-pent-4-enyl)indenyl)ethane
- 1-(9-fluorenyl)-2-(1-(3-hex-5-enyl)indenyl)ethane
- 1-(9-fluorenyl)-2-(1-(3-hex-5-enyldimethylsilyl)indenyl)ethane
- 1-(9-fluorenyl)-2-(1-(3-benzyl)indenyl)ethane

Example 6

10

Preparation of Metallocenes

- The ligands of Examples 2, 4, and 5 were used to prepare metallocenes of zirconium and/or hafnium. The general process used involved dissolving 3 mmol of the ligand in 40 ml of diethylether and combining that with two equivalents of n-butyllithium provided via a 1.6M hexane solution and stirring for at least about eight
- 15 hours at room temperature. Then one equivalent of zirconium tetrachloride or hafnium tetrachloride was added and the mixture stirred overnight. Further processing was conducted according to the solubility of the product: for soluble complexes, the mixture is filtered directly from the thus produced lithium chloride; for less soluble complexes, either the solvent is evaporated and the residue extracted with methylene
- 20 chloride, or the complex was filtered over sodium sulfate and the product extracted with methylene chloride or toluene from the first and then the solvent was evaporated under vacuum.

- Such a technique was also used to produce a metallocene using niobium pentachloride. The metallocene produced can be named 2-(9-fluorenylidene)-2-(1-(3-
- 25 (3-butenyl)indenylidene) propane niobium trichloride.

Example 7

Ethylene Polymerizations

- Various zirconium containing metallocenes were then evaluated to compare their effectiveness in the polymerization of ethylene. The polymerizations
- 30 were conducted in a laboratory autoclave with 1 liter reaction volume. For each polymerization the autoclave was filled with 500 ml of pentane and 7 ml of methylaluminoxane. A catalyst solution was prepared by combining the respective

- 10 -

metallocene with methylaluminoxane and toluene to produce a solution containing about 0.2 to about 0.5 mg of the metallocene per ml of toluene. Generally approximately 1 mg of the metallocene was employed in each polymerization.

5 In some case smaller amounts of metallocene were employed when it was recognized that the catalyst was extremely active. The autoclave was thermostated at 60°C and ethylene was added to maintain a pressure of 10 bar while the reactor contents were stirred. The polymerization was terminated by venting the reactor. The reaction time was generally about 1 hour but varied for some runs because of the difference in activities of the catalysts.

10 A summary of the results obtained is provided by the following tables wherein ligands having similar bridging groups are grouped together in separate tables. In the tables the polymerizations were for 1 hour unless indicated otherwise. The molecular weight of the polymers was compared using intrinsic viscosity (M_n) which was determined in cis/trans decal using an Ubbelohde precision capillary viscometer at
15 135+/- 0.1°C. Prior to the measurement, the polymer samples were weighed in sealable small flasks and dissolved in an exactly measured amount of decalin at 140-150°C over a period of three to four hours. Insoluble components were separated using hot filtration over glass wool. The intrinsic viscosity values were determined using available calibration curves.

<i>Table 1</i>			
<i>Dimethyl Methylene Bridged</i>			
R ¹	Activity	M _n	M _p
H	4200	100,000	135
5 Me ₃ Si-	16670	265,000	137
(allyl)Me ₂ Si-	19200	375,00	135
allyl	6300	240,000	133
3-butenyl	10200	300,000	133
4-pentenyl	17100	375,000	131
10 5-hexenyl	30900	340,000	137
butyl	35500	340,000	141
hexyl	24100	340,000	139
benzyl	14200	320,000	138
2-phenylethyl	25000	335,000	135
15 2-methoxyethyl	n.d.	210,000	132

Table 2***Phenyl Methyl Methylene Bridged***

R ¹	Activity	M _n	M _p
H	10400	185,000	134
Me ₃ Si-	53700	720,000	138
(allyl)Me ₂ Si-	11000 ^f	800,000	137
allyl	6200	580,000	134
3-butenyl	8800 ^g	750,000	136
4-pentenyl	16600 ^d	850,000	135
5-hexenyl	6900 ^h	770,000	136
butyl	21600	620,000	138
hexyl	14500	620,000	139
benzyl	70000	680,000	133
2-phenylethyl	34100 ^j	500,000	134

^d based on 120 minutes^f based on 25 minutes^g based on 140 minutes^h based on 90 minutes^j based on 20 minutes**Table 3*****1-Methyl-2-(1-Butenyl)Methylene Bridged***

R ¹	Activity	M _n	M _p
H	4400	210,000	133
Me ₃ Si-	23822	300,000	137
3-butenyl	n.d.	410,000	137

<i>Table 4</i>			
<i>Dimethyl Silyl Bridged</i>			
R ¹	Activity	M _n	M _p
H	8700	310,000	n.d.
#allyl	38200	350,000	134
3-butenyl	57000	330,000	137
4-pentenyl	90000	380,000	141
##5-hexenyl	26100	385,000	138
*5-hexenyl Me ₂ Si-	46000	380,000	138
butyl	33300	400,000	140
hexyl	39200 ^k	420,000	140
benzyl	138300 ^l	24,000	137

^k based on 45 minutes of polymerization

^l based on 15 minutes of polymerization

<i>Table 5</i>			
<i>Phenyl Methyl Silyl Bridged</i>			
R ¹	Activity	M _n	M _p
allyl	44,400	400,000	141
5-hexenyl	43100	275,000	138

Table 6***Diphenyl Silyl Bridged***

R ¹	Activity	M _n	M _p
H	21800	255,000	139
##allyl	26500	410,000	131
3-butenyl	54700 ^m	44,500	140
4-pentenyl	82800 ^j	430,000	141
##5-hexenyl	53500	480,000	135
(5-hexenyl)Me ₂ Si-	45800	420,000	137

^m based on 40 minutes of polymerization^j based on 30 minutes of polymerization**Table 7*****Control Examples - Unsubstituted Indenyl Ethylene Bridge, Fluorenyl and Branch Bonded At 1-position on Bridge***

Branch	Activity	M _n	M _p
3-butenyl	11500	330,000	135
5-hexenyl	9300	270,000	132
7-octenyl	17300	270,000	136

<i>Table 8</i>			
<i>Ethylene Bridged</i>			
R ¹	Activity	M _n	M _p
benzyl	110000 ^l	140,000	139
**allyl	153000	160,000	134
3-butenyl	198000 ⁿ	125,000	135
4-pentenyl	204000 ⁿ	180,000	140
**5-hexenyl	19800 ^j	15,000	136
*5-hexenyl Me ₂ Si	60800	180,000	136

^j based on 30 minutes

^l based on 45 minutes

ⁿ based on 10 minutes

Table 1 demonstrates that certain substituents at the 3-position on the indenyl result in a more active bridged indenyl/fluorenyl metallocene when the bridge is dimethyl methylene, i.e. isopropylidene. It also shows that the molecular weight was higher when the indenyl had a substituent in the 3 position.

A comparison of the control metallocene of Table 1 with the control of Table 2 demonstrates that the substitution of a phenyl group for one of the methyl groups of the bridge results in a more active catalyst. For many of the inventive metallocenes in Table 2 one does not see the dramatic improvement in activity over the control; however, the inventive metallocenes did produce polymers of much higher molecular weight. When the substituent on the 3 position of the indenyl was trimethyl silyl, 1-pentenyl, butyl, hexyl, benzyl, and 2-phenylethyl an improvement in activity was also noted.

Table 3 demonstrates that if the metallocene has a 1-methyl-1-(1-butenyl) methylene bridge a much more active catalyst is obtained if the indenyl has a trimethyl silyl group at the 3 position. Although the effect of a 1-butenyl group at the 3 position of the indenyl on the activity was not determined, the data also shows that such does result in a higher molecular weight polymer.

Table 4 demonstrates that substituents in the 3 position of the indenyl result in a much more active catalyst when the bridge is a dimethyl silyl bridge. The

- 16 -

polymers also were generally slightly higher in molecular weight. Table 5 shows that the corresponding metallocenes in which one methyl substituent on the bridge was replaced with a phenyl group are even more active. Table 6 shows the results obtained using an indenyl/fluorenyl metallocene bridged by a diphenyl silyl group. Again those
5 having a substituent at the 3 position on the indenyl were more active. Especially notable in Tables 4 and 6 is the activity obtained when the indenyl group is substituted in the 3 position by 1-pentenyl.

Table 7 should be compared with Table 8. The comparison shows that the inventive ethylene bridged metallocenes of Table 8, which have no branch on the
10 bridge but which have a substituent in the 3 position of the indenyl are much more active than the catalysts of Table 7.

Example 9

Self Immobilization of Catalyst

The metallocenes of the above examples were also evaluated to
15 determine their ability to copolymerize with ethylene to form a prepolymerized particulate catalyst. The evaluations were conducted in Schlenk tubes. Approximately 10 mg of the metallocene was combined with about 10 ml of a 30 weight percent solution of methylaluminoxane in toluene and further diluted with 40 ml of toluene and exposed to an ethylene pressure of 0.4 to 0.6 bar. The insertion of the metallocene
20 into the polymer chains was indicated by the characteristic coloration of the produced polymer precipitate.

The metallocenes having an omega olefin substituent were much more suitable for forming prepolymerized catalyst systems than those not containing such a substituent. The most effective were those having either a pentenyl or a hexenyl
25 substituent at the 3 position on the indenyl.

#The compounds of formula I wherein R¹ is allyl or propenyl and R is dimethylsilyl are shown in EP-A-729978, published September 4, 1996. One such compound is listed as the second compound of Table 4 above.

##The compounds of formula I wherein R¹ is 5-hexenyl and R is
30 dimethylsilyl and compounds of formula I wherein R¹ is allyl or 5-hexenyl and R is diphenylsilyl are disclosed in U.S. Serial No. 08/779,496, filed January 8, 1997, and in corresponding patent applications in certain other countries. Three such compounds

are indicated in Tables 4 and 6.

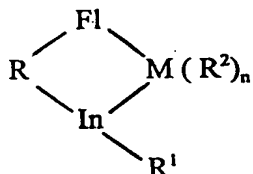
*The compounds of formula I wherein R¹ is 5-hexenyldimethylsilyl and R is dimethylsilyl or ethylene are disclosed in U.S. Serial No. 08/779,497, filed January 8, 1997. Two such compounds are listed as the sixth compound of Table 4 and as the last compound of Table 8.

**The compounds of formula I wherein R¹ is allyl or 5-hexenyl and R is ethylene are disclosed in U.S. Serial No. 08/781,587, filed January 8, 1997. Two such compounds are listed as the third and the sixth compounds of Table 8.

- 18 -

CLAIMS

1. A bridged fluorenyl/indenyl containing metallocene of the formula:



wherein R is a divalent organo radical connecting Fl and In, Fl is a 9-fluorenyl radical, In is an indenyl radical connected to R at the 1 position and to R¹ at the 3 position, wherein In has no further substituents, wherein R¹ is an alkyl, an aralkyl, an alkenyl, an alkyl silyl, an alkenylsilyl or an alkoxyalkyl radical having 1 to 20 carbon atoms, M is a metal which is titanium, zirconium, hafnium, niobium or tantalum, and each R² can be the same or different and is hydrogen, a halide, an alkyl radical containing 1 to 10 carbon atoms, an aryl radical having 6 to 12 carbon atoms, an alkenyl radical having 2 to 10 carbon atoms, an arylalkyl radical having 7 to 40 carbon atoms, an arylalkenyl radical having 8 to 40 carbon atoms, or an alkylaryl radical having 7 to 40 carbon atoms, n is a number to fill the remaining valences of M, further subject to the proviso that R¹ is not allyl or propenyl if R is dimethylsilyl.

2. A metallocene according to claim 1, wherein R is a divalent radical which is dimethyl silyl, diphenyl silyl, phenyl methyl silyl, dimethyl methylene, 1-methyl-1-phenyl methylene, diphenyl methylene, an alkenyl substituted ethylene having 4 to 12 carbons, an alkyl substituted ethylene having 4 to 12 carbons, or 1,2-ethylene.

3. A metallocene according to claim 1, wherein R¹ is a radical which is a trialkyl silyl having 3 to 12 carbon atoms, an omega-alkenyl-1,1-dimethyl silyl in which the alkenyl group contains 2 to 10 carbon atoms, an omega-alkenyl having 2 to 10 carbon atoms, or an alkyl having 1 to 10 carbon atoms.

4. A metallocene according to claim 3, wherein M is zirconium, n is 2, and R² is Cl.

5. A metallocene according to claim 4, wherein R dimethyl silyl or diphenyl silyl.

6. A metallocene according to claim 5, wherein R¹ is an omega-alkenyl radical having 4 to 6 carbon atoms.

7. A metallocene according to claim 6, wherein R¹ is 1-pentenyl.

8. A metallocene according to claim 7, wherein R is diphenyl silyl.
9. A metallocene according to claim 4, wherein R is dimethyl methylene or phenyl methyl methylene.
10. A metallocene according to claim 9, wherein R¹ is trimethyl silyl, an
5 omega-alkenyl having 3 to 6 carbon atoms, or an omega-alkenyl dimethyl silyl wherein the alkenyl group has 3 to 6 carbon atoms.
11. A metallocene according to claim 10, wherein R¹ is 4-pentenyl.
12. A metallocene according to claim 11, wherein R is phenyl methyl methylene.
- 10 13. A metallocene according to claim 10, wherein R is dimethyl methylene.
14. A metallocene according to claim 13, wherein R¹ is 5-hexenyl dimethyl silyl.
15. A metallocene according to claim 10, wherein R is phenyl methyl methylene.
- 15 16. A metallocene according to claim 4, wherein R is ethylidene.
17. A metallocene according to claim 16, wherein R¹ is an omega-alkenyl having 4 to 6 carbon atoms.
18. A metallocene according to claim 1, wherein R is methyl omega-alkenyl methylene wherein the omega-alkenyl has 4 to 6 carbon atoms.
- 20 19. A metallocene according to claim 18, wherein R is methyl omega butenyl methylene.
20. A metallocene according to claim 19, wherein R¹ is an omega-alkenyl.
21. A metallocene according to claim 20, wherein R¹ is 3-but-3-enyl.
22. A process for producing a polymer which comprises contacting at least
25 one olefin with a metallocene according to any one of the preceding claims, under suitable polymerization conditions.
23. A process according to claim 22, wherein ethylene is polymerized and methylaluminoxane is used as a cocatalyst.
24. A process according to claim 23, wherein R is ethylidene.
- 30 25. A process according to claim 24, wherein R¹ is an omega-alkenyl radical having 4 to 6 carbon atoms.
26. A process according to claim 23, wherein R is methyl (omega- alkenyl)

methylene.

27. A process according to claim 23, wherein R is dimethyl methylene.
28. A process according to claim 27, wherein R¹ is 3-hex-5-enyldimethyl silyl.
- 5 29. A process according to claim 27, wherein R¹ is 3-pent-4-enyl.
30. A process according to claim 27, wherein R¹ is an omega-alkenyl having 4 to 6 carbon atoms.
31. A process according to claim 30, wherein R is diphenyl silyl.
32. A process according to claim 30, wherein R is dimethyl silyl.
- 10 33. A process according to claim 23, wherein said polymerization is conducted using a catalyst system prepared by prepolymerizing said metallocene in the presence of aluminoxane and a particulate solid to obtain a particulate solid active as a polymerization catalyst.
34. A process for producing a bridged fluorenyl/indenyl ligand having a
15 substituent at the 3-position of the indenyl, which comprises reacting lithium fluorenyl with a benzofulvene in diethylether to produce a bridged fluorenyl/indenyl ligand lithium salt and then reacting said ligand lithium salt with an organic halide which is an alkyl halide, an alkenyl halide, or an organosilyl halide.
35. A process according to claim 34, wherein the organic halide is an alkyl
20 halide having 1 to 10 carbon atoms, an omega-alkenyl-1,1-dimethyl silyl halide in which the alkenyl group contains 2 to 10 carbon atoms, or an omega-alkenyl halide having 2 to 10 carbon atoms.
36. A process for preparing a bridged fluorenyl/indenyl metallocene, which comprises reacting a bridged fluorenyl/indenyl ligand when made by a process
25 according to claim 34 or 35, with an alkyl lithium to produce the lithium salt and then reacting the lithium salt with a transition metal halide wherein the metal is titanium, zirconium, hafnium, niobium, or tantalum.
37. A compound according to claim 1, wherein R¹ is not 5-hexenyl when R is dimethyl silyl and R¹ is not allyl or 5-hexenyl when R is diphenyl silyl.
- 30 38. A compound according to claim 37, wherein furthermore R¹ is not (5-hexenyl)dimethylsilyl when R is dimethylsilyl or ethylene and R¹ is not allyl or 5-hexenyl when R is ethylene.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/13095

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C07F 7/08, 7/28, 7/00, 9/00; C08F 4/44, 4/642

US CL : 556/11, 12, 43, 53; 526/127, 160, 943

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 556/11, 12, 43, 53; 526/127, 160, 943

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,T,P	US 5,770,753 A (KUBER et al.) 23 June 1998, see entire document.	1-38
A,T,E	US 5,786,495 A (RESONI et al.) 28 July 1998, see entire document.	1-38

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

03 DECEMBER 1998

Date of mailing of the international search report

30 DEC 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

PAUL F. SHAVER

Telephone No. (703) 308-0196